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# Multi-functionalization Of Silicon By Nanoparticles Through "Plug and Play" Approach

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## ABSTRACT

In this paper, we demonstrate a "Plug and Play" approach, whereby externally synthesized nanoparticles of desired functions and size are incorporated into the semiconductor, followed by the manipulation of surface chemical bonds in order to achieve multiple functionality. Sonochemically synthesised $Fe_2O_3$ nanoparticles were introduced onto device quality Si wafers. On annealing the particle-treated Si wafer in ultra high vacuum, oxygen changes the bonding partner from Fe to Si and desorb as SiO at ~ 760°C, leading to the formation of uniform sized Fe nanoparticles ( size ~6-8 nm) on the surface and the sample shows ferromagnetic behaviour. More importantly, the particle treated Si exhibits light emission at wavelengths 1.57, 1.61 and 1.65 microns (full width at half maximum ~ 20 meV). Emission in this wavelength range is crucial for optical communications and is highly desired from a Si based material. Further, oxidation of this material leads to the formation of a selective capping layer of $SiO_2$. Thus, by manipulating the surface chemical bonds, we are able to introduce optical, magnetic, metallic and insulating functions to Si. Additionally, the particles exhibit self-assembly on a patterned Si surface. We believe that this approach is universal and the material developed here is compatible with the planar Si technology, bringing us closer to realization of Si based monolithic electronics.

## INTRODUCTION

Realization of nanoscale devices depends crucially on the successful fabrication of nanostructures and their functionalization. Techniques such as, lithography, self-organization, atom manipulation using scanning tunneling microscope tip, chemical bond manipulation, control and design of surface atomic steps, or a combination of some of these, are employed to achieve these goals [1-4]. However, there are major problems encountered in these approaches which limit the advancement in this field. They are mainly associated with the poor controllability of the size, positioning as well as the functionality of the nanostructures. In order to ovecome these problems, we propose a "Plug and Play" approach, where externally synthesized nanoparticles of desired functions and size are incorporated into the semiconductor, followed by the manipulation of surface chemical bonds. This would enable fabrication of tailor-made structures on the whole wafer surface. In this paper, we demonstrate this idea, by taking the example of the interaction of $Fe_2O_3$ nanoparticles with device quality Si, Ge wafers and graphite.

## EXPERIMENTAL

Sonochemically synthesised $Fe_2O_3$ nanoparticles (spherical shape, size ~6-8 nm) [5] were introduced onto device quality Si wafers, from an ethanol suspension, kept in ultrasonic bath for a period of 30 min. They are rinsed in running water and dried with nitrogen gas. Si wafers are prior cleaned chemically. These samples are introduced into ultrahigh vacuum chamber (UHV) and degassed at around 100°C for a couple of hours. The samples are heated to a particular temperature and kept for 15-20 min. and the photoemission measurements are performed at room temperature. For achieving complete reduction, final anneal was performed at around 850°C for 3 min. In some cases, an ultrathin layer of Si was deposited onto this sample at around 500°C followed by anneal at 550°C for about 10-15 hrs. The samples are examined by a variety of other techniques, such as atomic force microscopy, photoluminescence, magnetic measurements, mapping of Auger signals, after taking it out of the chamber. The nature of the surface species was characterised *in-situ* by photoelectron spectroscopy. Samples were transferred to the molecular beam epitaxy (MBE) chamber where evaporation of Si was carried out by using an electron beam. The samples were examined, outside the chamber, by a variety of technique. Additionally, we have examined the surface transformation by employing highly surface sensitive synchrotron radiation photoelectron spectroscopy and the results will be published elsewhere 6

## RESULTS AND DISCUSSION

Figure 1 shows an AFM image of a planar Si(111) which was treated with the nanoparticles and subsequently annealed in UHV at 850°C. As can be seen, the particles are of uniform size and nucleate at step edges and annealing results in the etching of Si as SiO species and leads to the reduction of the iron oxide to elemental Fe. The XPS results shown in figure 2 clearly indicate the occurrence of the reaction,

$$Fe_2O_3 + 3\,Si \Rightarrow 2\,Fe + 3\,SiO$$

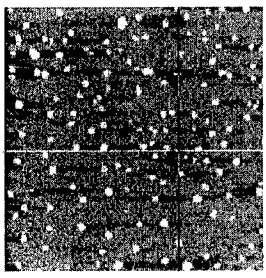

**Figure 1**

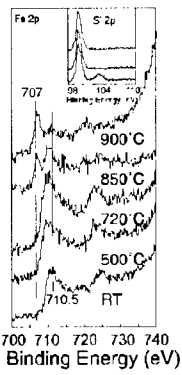


**Figure 2**

Figure 1 AFM image from the nanoparticle treated Si sample. The dot like structures are nanomagnets of Fe.

Figure 2 shows the thermal transformation of iron oxide particles by reaction with substrate silicon atoms

At these temperature and pressure the SiO is volatile and desorbs immediately, driving the reaction to completion, as is evident from x-ray photoelectron spectroscopy (Figure 2). The chemical shift in Fe $2p_{3/2}$ core level (3.5 eV) in the annealed sample, and the disappearance of the signal due to oxygen in Si 2p as well as O 1s regions, unequivocally establish the occurrence of this reaction. In essence, this reaction is similar to the reduction of iron oxide by carbon in the preparation of steel at ~1500°C. However, in the case of a surface reaction, the temperature is reduced due to desorption of SiO species. Interestingly, we have observed complete reduction of $Fe_2O_3$ nanoparticles to Fe at 450°C when deposited on Ge surfaces. Thus, the temperatures in which SiO and GeO species desorb dictate the reduction temperature in the Si and Ge cases, respectively.

Figure 3 depicts the photoluminescence (PL) spectrum recorded from this sample, showing sharp emission at three wavelengths—excited by He-Ne laser—1.57, 1.61 and 1.65 μm. This is the first report on multiple and narrow width light emission from a well-defined and device compatible Si based material that is of great significance for fiber optics communications [7]. Although weak, there is emission even at room temperature (RT). The emission at 1.57 □m originates from traces of the semiconducting silicide, β-$FeSi_2$, which is formed by the reaction of $Fe^o$ and $Si^o$. The β-$FeSi_2$, a covalent and environmentally friendly semiconductor possessing a direct bandgap (Eg ~ 0.8 eV), has been a topic of intense study recently as a candidate for a Si-based light emitter. [8-11]. They employed the method of implanting Fe ions into Si wafers and formed precipitates of iron silicide of various sizes. [11]

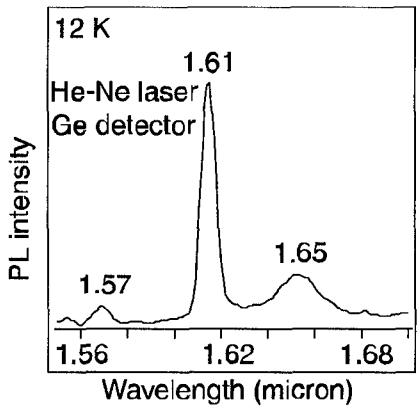


Figure 3

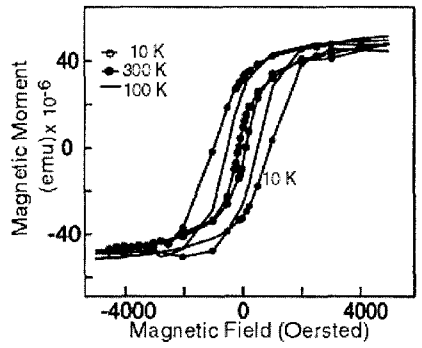


Figure 4

Figure 3. PL spectrum recorded from the nanoparticle treated Si sample at 12 K. Figure 4. Magnetization data measured on the nanoparticle treated Si sample at various temperatures, clearly showing the ferromagnetic behaviour. Hysteresis loop opens at low temperature

The emission intensity could be further increased by depositing a thin overlayer of Si, using molecular beam epitaxy (MBE) mode, followed by annealing at 530°C for several hours. The reflection high-energy electron diffraction monitored *in situ* during the Si MBE and subsequent annealing provides support for this reaction. The emission intensity decreased on raising the sample temperature, suggesting that the process is thermally activated, and indicating that the origin is exciton related. The observation of features at similar energies in the absorption spectrum from these samples supports this view. However, further measurements are required to fully understand the emission mechanism from this novel material. We have fabricated a series of samples by a variety of methods (such as Fe deposited or Fe implanted into Si, and nanoparticle treated Ge), examined the PL spectra, and found that none other than the nanoparticle-treated Si exhibits this behaviour. Secondary ion mass spectroscopy (SIMS) failed to detect any Fe diffused into the bulk.

The Si wafer with the as-incorporated amorphous $Fe_2O_3$ particles exhibits superparamagnetic behaviour, which is characteristic of amorphous nanoparticles. However, after annealing, the samples show soft ferromagnetic property as shown in Figure 4. This behaviour is attributed to the fact that the oxide particles are transformed to crystalline nanoparticles of Fe. The magnetic measurements were performed using a superconducting quantum interference device (SQUID). It was observed that the coercivity increases when the sample temperature is lowered to 10 K. This type of material might have tremendous impact in the area of magnetic semiconductors or spintronics and memory devices [12,13] . We have further introduced insulating features to this material by oxidation, which results in the preferential formation of an $SiO_2$ capping layer, thus preserving the light emitting and magnetic properties. The nanoparticles exhibit self-assembly on patterned Si wafers. Figure 5 shows that the periphery of the dot and trench patterns is decorated by uniform sized nanoparticles. This is due to their preferential nucleation on reactive centres in the step-bunched regions. Element mapping of the SEM image performed micro-Auger mapping indicates that these structures consist predominantly of elemental Fe.

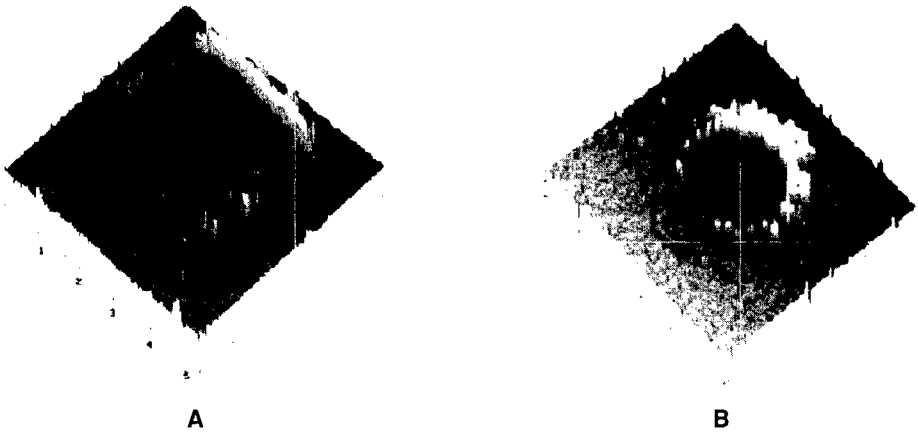


Figure 5 Self-organization of Fe nanoparticles formed by the reduction of iron oxide particles on patterned silicon substrates A and B are dot and trench patterns

In conclusion, we have demonstrated, for the first time, that manipulating the properties of amorphous $Fe_2O_3$ nanoparticles on Si results in multiple light emission (narrow fwhm) and multiple functionality (magnetic, metallic, semiconducting, insulating, and optical) and clearly show an "all in one" or "all from one" approach. The amorphous $Fe_2O_3$ nanoparticle changed their properties from superparamagnetic to soft ferromagnetic by their reduction to metallic Fe. The subsequent reaction of $Fe^0$ with $Si^0$ results in the formation of β-$FeSi_2$, a semiconductor that emits light in wavelengths that are critical for fiber optics communication. The spatial distribution of the nanoparticles could be controlled by proper patterning of the Si wafer. While ion beam synthesis, which introduces a large number of defects in the Si substrate, this "plug and play" approach is compatible with the existing planar Si technology, and therefore is a promising candidate for realising monolithic integration of optical and magnetic features along with integrated circuits.

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